

Peculiarities of Spin Polarization Inversion at a Thiophene/Cobalt Interface

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We perform *ab-initio* calculations to investigate the spin polarization at the interface between a thiophene molecule and cobalt substrate. In contrast to the expected spin polarization inversion [N. Atodiresei et al., Phys. Rev. Lett. **105**, 066601 (2010)], the reduced symmetry in the presence of a sulfur atom leads to a strong spatial dependence of the spin polarization of the molecule: The two carbon atoms far from the sulfur acquire a polarization opposite to that of the substrate, while the carbon atoms bonded directly to sulfur possess the same polarization as the substrate. We determine the origin of this peculiar spin interface property as well as its impact on the spin transport.

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The discovery of spin-related phenomena in organic materials promises exciting development towards low cost yet efficient spintronic devices [1, 2]. In the focus is the study of novel properties combining traditional inorganic and the organic materials, such as the interface between an organic molecule and a ferromagnetic metal, the so-called *spininterface* [3]. A key ingredient to spin manipulation in such a hybrid structure is spin injection, which continuously demands higher efficiency and better understanding [4–6]. Therefore, the behaviour of the spin at a spininterface is of great importance to unravel the mysteries of spin transport in hybrid systems. Experimentally, spin-polarised scanning tunneling microscopy [7] has been shown to be a highly successful tool to provide detailed spin information at a surface [8, 9]. Despite numerous experiments, not many theoretical efforts have been put forward to scrutinize the uniqueness of a spininterface, where the level of complexity places a challenge to simple analytical models. On the other hand, *ab-initio* calculations provide a well established platform to deepen the understanding of complex systems.

Recently, for a group of carefully selected molecules of similar electronic properties, Atodiresei *et al.* have carried out an *ab-initio* study towards the interface formed by organic molecules adsorbed on a ferromagnetic Fe/W(110) surface [10]. A polarization inversion on the molecular side has been found, which is consistent with experimental results using spin-polarised scanning tunneling microscopy: the sign of the spin polarization of the molecule is opposite to that of the substrate to which it is chemically bonded. The selection of the molecules is based on the $\pi(p_z)$ electron systems which usually have a strong interaction between the π electrons of the molecule and the d orbitals of the ferromagnetic substrate, thus allowing a Zener-type exchange interaction (between the p_z and d orbitals) to trigger the polarization inversion. The selected molecules (C_5H_5 , C_6H_6 , and C_8H_8), from the molecular structure point of view, are highly symmetric in the molecular plane and composed of only carbon (C) and hydrogen (H) atoms. For example, the C_5H_5

molecule is a unit of an even larger molecule as compared to H_2Pc .

In this Letter, we report a peculiar picture of spin polarization inversion as a result of asymmetry in the molecular structure on the functionality of p_z - d exchange. We perform *ab-initio* calculations to investigate an organic-ferromagnetic metal interface formed by a thiophene (C_4H_4S) molecule adsorbed on a cobalt (Co) substrate. The motivations for this choice are as follows. Besides serving as the basis unit to form polythiophene (such as α -sexithiophene, commonly known as T6 molecule) that is widely used in organic spintronics [1], the thiophene molecule is less symmetric than C_5H_5 since one C is substituted by an S atom. The impact of the reduced symmetry on the local spin polarization at a spininterface is yet to be explored. A small molecule with a relatively simple composition, like thiophene, gives us the advantage to concentrate on the significance of a particular critical mechanism, such as the Zener exchange scrutinized in this paper. Moreover, the delocalized electron pairs of sulfur in the π electron system render the reactivity of thiophene to be comparable (though less) to molecules like C_5H_5 . Moreover, a T6 molecule consists of six thiophenes bonded linearly through the 2- and 5-positions. We expect the spin interface properties associated with a thiophene molecule to persist into the chain, thus having direct implications for T6 molecules.

The structure is shown in Fig.1. A thiophene molecule is placed on the Co(001) surface. Before the structure relaxation, the initial position of the molecule on the Co surface is selected to be as symmetric as possible with respect to the S atom to minimize the total force. We next perform a charge relaxation to allow the force exerted on the molecule to be minimal. As shown in Figs. 1(c) and (d), after the structure relaxation the molecule plane is no longer flat: the S-Co bond becomes longer than in its initial configuration. Full-potential linearized augmented plane wave calculations are performed using the WIEN2k package [11]. To simulate the Co(001) surface, we employ a slab geometry with a 3×3 in-plane surface unit cell and

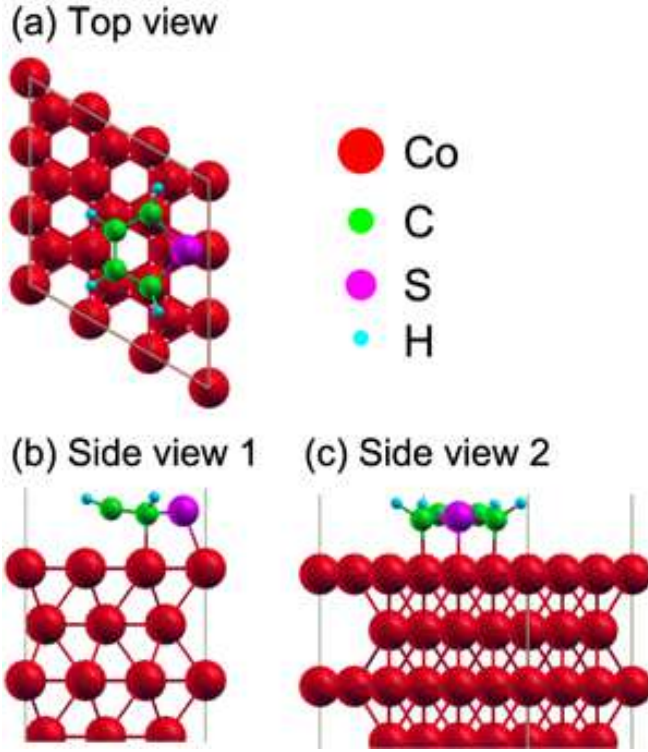


FIG. 1. (color online). A thiophene molecule adsorbed on a Co(001) surface after structure relaxation.

eight Co atomic layers that are terminated by a vacuum layer of 18 Å. A threshold energy of -6.0 Ry, which separates valence and core states, is used in all calculations. We employ for the muffin-tin radius R_{mt} values of 2.2 bohr, 1.2 bohr, 1.5 bohr and 0.7 bohr for Co, C, S and H, respectively. A small value of $R_{\text{mt}}K_{\text{max}} = 2$ is used due to the H atoms in the system [11]. The k -mesh is set to be $6 \times 6 \times 1$ and all calculations are conducted with the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation to the exchange correlation potential [12]. Force convergence of 5 mRy/bohr is employed in the structure relaxation. In systems consisting of macromolecules (such as CoPc) [9], long range van der Waals forces can be relevant for the relaxation and, thus, for the spin polarization. However, in the present setup they are not decisive and will be omitted in the calculations. We find a strong chemical bonding between the molecule and the substrate, which dominates the van der Waals forces by several orders of magnitude. Similar findings have been reported for related molecules [10].

For the purpose of comparison, we show in Fig. 2(a) the spin-polarized local density of states of a Co atom in a clean surface. Figure 2(b) depicts the density of states averaged over the 4 Co atoms below the thiophene molecule. By comparing panels (a) and (b), the out-of-plane $d_{3z^2-r^2}$, d_{xz} , and d_{yz} orbitals of Co are modified due to the coupling to the p_z orbital of C. The in-plane $d_{x^2-y^2}$ and d_{xy} orbitals are much less affected. This sug-

gests that the hybridization scheme in the present case is similar to the interface between Fe and the big $\pi(p_z)$ molecules [10]. Being a neighbor to Fe ($3d^64s^2$) in the periodic table, the electron configuration of Co is $3d^74s^2$. Figure 2 also shows that the change is much less dramatic for the spin-up states than for the spin-down states. Therefore, we expect that the hybridization scheme exhibited in Fig. 2 accommodates a p_z - d Zener exchange interaction that eventually gives rise to a spin polarization inversion on the molecule.

For the molecule, Fig. 3 shows the density of states of the entire molecule in panel (a), of the C atoms in panels (b) and (c), and of the S atom in panel (d). In contrast to a C_5H_5 molecule, the reduced symmetry of thiophene motivates us to divide the C atoms into two groups: in group C2 (the so-called 2- and 5-positions) the C atoms are adjacent to S, while group C1 comprises the other atoms (3- and 4-positions). At the Fermi energy, the out-of-plane p_z orbital exhibits a very small spin imbalance as the spin up state slightly dominates. In contrast, on the Co site the spin down states dominate, which suggests that indeed a spin polarization inversion takes place, but at an insignificant magnitude. Interestingly, around 1.5 eV below the Fermi energy, the spin up $d_{3z^2-r^2}$ peak of Co (below the thiophene) echoes the spin up S peak at the same energy. In addition, the spin down $d_{3z^2-r^2}$ peak of Co reappears in the spin down density of states of the C1 group. Both peaks do not appear for the C2 group.

We plot in Fig. 4 the local spin polarization at the *interface* and *surface*, which constitutes the main results of this Letter. The interface is defined as a plane located between the thiophene molecule and the Co surface, about 0.9 Å below the molecule. The surface is defined as a plane 0.9 Å above the molecule. The spin polarizations at the interface and surface have direct implications for the spin transport across the interface and for scanning tunneling microscopy. Figure 4 reveals an interesting polarization inversion: at the interface (Fig. 4(a)) the two C atoms at the 2- and 5-positions (C2 group) are polarized in the same direction as the substrate, while the two C atoms at the 3- and 4-positions (C1 group) are polarized in the opposite direction. This reflects a polarization inversion, yet with a rather small magnitude. At the surface (Fig. 4(b)) we find for the two C2 atoms barely any polarization, while for the two C1 atoms a small reversed polarization appears.

As a matter of fact, our results suggest that the p_z - d exchange interaction proposed in Ref. [10] is a viable mechanism to induce polarization at a spinterface, but it is the detailed structure of the molecule that determines the polarization inversion scheme. To explain the peculiar polarization shown in Fig. 4, we first need to address the effect of a reduced symmetry. In the present case of thiophene on Co, the substitution of a C atom (from the C_5H_5 molecule) by an S atom breaks the symmetry that is maintained in a π electron system consisting of only C

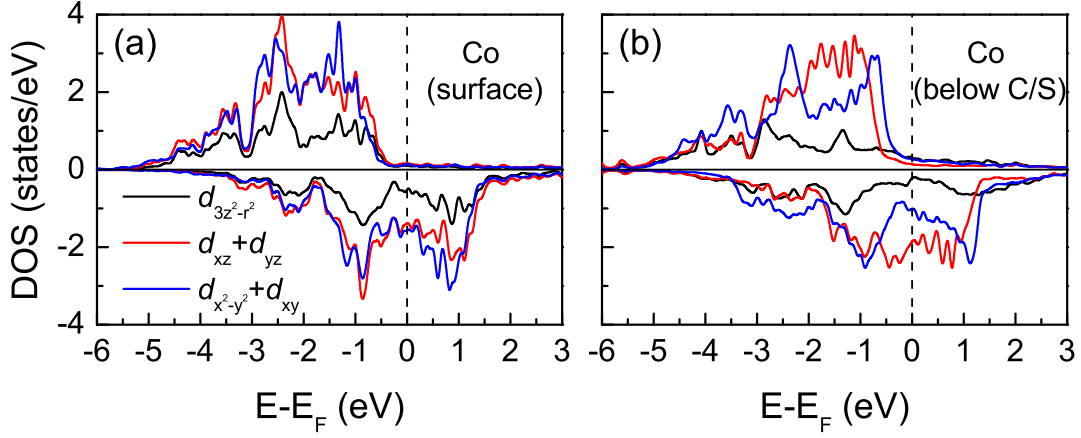


FIG. 2. (color online). Density of states (a) of a Co atom on a clean surface and (b) averaged over the 4 Co atoms below the C/S atoms of the thiophene molecule.

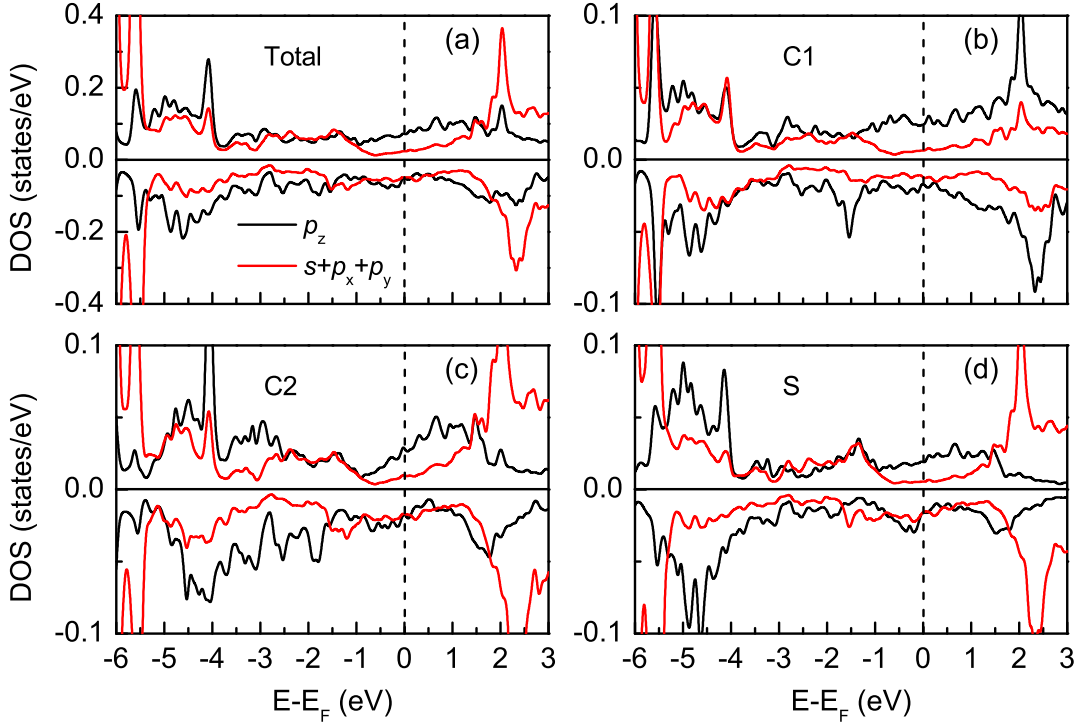


FIG. 3. (color online). Density of states of (a) the entire thiophene on the Co(001) surface, (b) the two C atoms at the 3- and 4-positions (C1 group), (c) the two C atoms at the 2- and 5-positions (adjacent to the S atom; C2 group), and (d) the S atom.

and H, thus naturally dividing the C atoms into C1 and C2 groups. The magnitude of the p_z - d exchange coupling depends critically on the overlap between the p_z and d orbitals. In the case of C_5H_5 on Fe, all five C atoms feel more or less the same orbital overlap. We therefore expect a rather uniform spatial distribution of the spin polarization. By its spatially more extended orbitals, a S atom interacts with the C1 and C2 atoms differently. The p_z - d bonding is more distorted for the C2 atoms than for the C1 atoms, rendering a much smaller p_z - d overlap

on C2 and, thus, suppressing the inversion effect due to the p_z - d exchange. Being far from the S atom, the C1 atoms enjoy larger orbital overlaps, leading to larger exchange coupling and polarization inversion. It is difficult to estimate the magnitude of the exchange coupling in the present setup. However, our results and qualitative picture based on symmetry suggest that the exchange coupling in the thiophene on Co system is smaller than what has been obtained for C_5H_5 on Fe [10]. The results presented in this Letter reflect an intriguing pic-

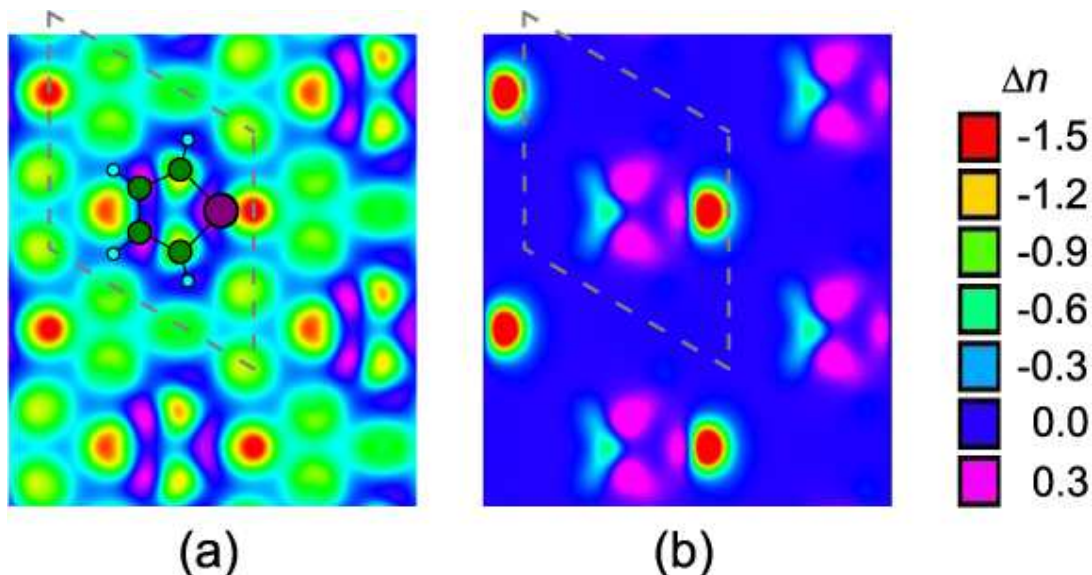


FIG. 4. (color online). Local spin polarization Δn (10^{-3} e/bohr³), defined as the difference between the spin up and spin down electron densities, at (a) the interface between the substrate and the thiophene and (b) the surface above the thiophene.

ture in terms of microscopic spin transmission through the interface: depending on the route through which an electronic spin enters the molecule, it either confronts a parallel (through C2 group) or antiparallel alignment (through C1 group) of the local moment.

In conclusion, we have performed *ab-initio* calculations to investigate the spin polarization inversion at the interface between a thiophene molecule and cobalt surface. In the thiophene molecule, we have obtained a spin polarization inversion for the two C atoms located far from the S atom, while neighboring C atoms show no inversion. Our first principles results and symmetry arguments demonstrate that, although the p_z - d Zener exchange qualitatively explains the spin polarization inversion, the viability of such a mechanism is governed by the detailed structure of the organic molecule.

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